Russian Journal of General Chemistry 2006 vol.76 N3, pages 430-436

Synthesis and properties of phosphabetaine structures: IV. 3-(triphenylphosphonio)propanoate in reactions with dipolar electrophilic reagents

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Abstract

Reactions of 3-(triphenylphosphonio)propanoate with heterocumulenes, such as phenyl isocyanate and dicyclohexylcarbodiimide, we studied under the assumption that they proceed by nucleophilic addition and 1,4-dipolar cycloaddition schemes. Quantum-chemical calculations show that the σ5-phosphorane cycloadduct of the betaine with isocyanate is thermodynamically preferred over its isomeric zwitter-ionic adduct. However, the experimental evidence suggests that the reaction with phenyl isocyanate involves nucleophilic addition of the betaine to isocyanate followed by hydrolysis to firm finally a complex of the starting betaine with diphenylurea. The structure of the complex was established by X-ray diffraction analysis. The revealed above controversy is explained by a high protophilicity of betaine structures, which is also confirmed by the results of the reaction of the betaine with carbodiimide. © Pleiades Publishing, Inc., 2006.

http://dx.doi.org/10.1134/S1070363206030133